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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
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INVESTIGATIONS ON AMERICAN PETROLEUM.

BY CHARLES F. MABERY.

XXVI. — *ON THE BUTANES AND OCTANES IN
AMERICAN PETROLEUM.*

BY CHARLES F. MABERY AND EDWARD J. HUDSON.

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XXVI. — ON THE BUTANES AND OCTANES IN
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BY CHARLES F. MABERY AND EDWARD J. HUDSON.

Presented October 14, 1896.

As one of us (C. F. M.) has shown † the form of the butanes and octanes in American petroleum is not so well understood as other constituents of the series C_nH_{2n+2} . Concerning the butanes, except that an analysis of a gas condensed at 0° by Ronalds gave the composition required for butane, very little has been published beyond the fact that distillates have been collected at 0° and at 8° – 9° . It, therefore, seemed advisable to devote some time to the separation of the butanes for the purpose of ascertaining with greater precision what hydrocarbons with these boiling points are actually contained in petroleum.

THE BUTANES.

The early investigations of Pelouze and Cahours ‡ indicated the presence of butane in their most volatile distillates. A portion collected between 5° and 10° gave with chlorine a "chlorbutyl," boiling point 65° – 70° . In a higher distillate, whose boiling point was not given, amyl hydride was suspected by the formation of a "chloramyl" boiling at 95° – 103° , but this hydrocarbon was not further identified. In the first analysis of the gas from Pennsylvania petroleum, Ronalds § condensed an oil at 0° – 1° , specific gravity 0.6000 at 0° , that gave the composition

* For efficient aid in the work of this paper, I should acknowledge my obligations to Mr. W. H. Whitfield, who selected portions of the work on the butanes as the subject of a thesis for the degree of Bachelor of Science, and to my assistants, Messrs. C. A. Soch and E. Davidson. — C. F. M.

† Proc. Amer. Acad., XXXI. 23.

‡ Compt. Rend. 1862, p. 1241.

§ London Chem. Soc., 1865, p. 54.

required for butane. Ronalds also collected an oil between 6° and 8° , specific gravity 0.6004, vapor density 2.178, which he regarded as a mixture of butane with higher constituents. As will be shown in this paper, nothing further has been done toward verifying the pentane from which the pentyl chloride of Pelouze and Cahours was obtained, although it was really derived from the pentane boiling at 30° , as we have ascertained after many trials.

Probably on account of difficulty in procuring an adequate supply of material, Warren * gave less attention to the butanes than to the higher constituents. He collected a distillate at 0° , which, on the basis of Ronald's determination, he assumed was a butane. After repeated and careful distillation through his regulated condenser, Warren also separated a liquid, boiling point 8° – 9° . Although nothing further was done towards determining its composition, Warren believed this body "to have been sufficiently purified to justify the conclusion supported by analogy that there is a constituent boiling at about 8° – 9° ." Since no other attempts have been made to identify the butanes, further study of these bodies was evidently necessary.

In returning to this subject, we assumed at first that it would only be necessary to enforce the results already obtained, which seemed to be supported by our first determinations.† But as the work progressed, it soon became evident that this assumption would not be justified. Taking advantage of the extremely cold weather in January, 1895, through the kindness of Messrs. Schofield, Shirmer, and Teagle, we procured 45 litres of a second distillate of the naphtha from Pennsylvania and Ohio petroleum, the most volatile portion that could be condensed with the atmospheric temperature below 0° F. Since the naphthas from Pennsylvania and Ohio petroleum are re-distilled together, it is difficult to procure this portion from either crude oil, unless, indeed, a run of the crude oil were made in the refinery with this object in view. But this did not seem necessary, since there can be little doubt that the constituents of the most volatile portion of Ohio and Pennsylvania petroleums are identical. During the continued cold weather of January, February, and March of the same year, distillation of this product was continued through a Warren condenser, filled with a freezing mixture, and the temperature of the distillates was kept very low to avoid loss so far as possible. In this manner a long series of distillations was carried on with small loss, aside from transference, except of the most volatile distillates. In these volatile

* Proc. Amer. Acad., XXVII. 56.

† Ibid., XXXI. 23.

portions, -20° to -10° , the distillation proceeded from the heat of the surrounding atmosphere, and it was regulated by cooling the still. The results obtained in the study of these distillates were so unexpected, the entire process of distillation was repeated several times during the colder months of the present year until in all 250 litres of 88° and 92° gasoline have been distilled, the portions below 12° , twenty times. The interesting results in the distillations of the present year, especially in excluding a butane at 8° – 9° , are due to the patience and care of Mr. Whitfield.

In studying the derivatives of these hydrocarbons, the chlorine substitution products were first formed by bringing together chlorine and the vapor of the hydrocarbon. The method we employed differed somewhat in details from the method of Schorlemmer.* In the reaction between chlorine and the hydrocarbon, the intensity of light must be carefully regulated. In direct sunlight so much heat is developed that a flame appears with the separation of carbon. In a cloudy day the action proceeds slowly, and with less light it is suspended. We obtained the most satisfactory results both as regards the progress of the reaction and the yield of the monochlor derivative in clear sunshine with a sheet of newspaper interposed. In all our distillates the action of chlorine has proceeded with great readiness in the cold. The distillates collected below 0° were well cooled by means of a freezing mixture. The condensation of the chlorinated product was more complete in a capacious bottle, — a two-litre bottle for 100–200 c.c. of the oil, with the delivery tube extending half way from the top of the bottle to the surface of the liquid. The heavier chlorine comes into intimate contact with the vapor of the oil, and the product condenses for the most part on the side of the bottle. Some of it unavoidably escapes with the hydrochloric acid, and it may be condensed in part by placing in front another bottle well cooled, or still better by passing the escaping gas through water. We have not found it essential to separate by distillation the chlorinated product from the hydrocarbon until the action was finished. If it be stopped with a small amount of the hydrocarbon unchanged, which may easily be determined by experience, the product is nearly all the monochlor-compound. The use of iodine suggested by Schorlemmer has not seemed essential, at least in the formation of the butane derivatives, since, without it, there is no difficulty in obtaining 80 per cent of the monochlor-compound, the remainder consisting for the most part of unchanged hydrocarbon, nor in our experience

* Philosophical Transactions, CLXII. 111 (1872).

is the yield increased by the use of iodine. In the separation by fractional distillation of the products of the chlorination, our experience is not in accordance with that of Schorlemmer, who stated that neither the chlorides nor the acetates could be separated by distillation. With long continued distillation, as our results will show, the crude product of the chlorination may be separated into its constituents sufficiently to yield constant boiling points and satisfactory analytical data.

Since Beilstein* found that isobutane boils at $-17^{\circ}.5$, it seemed reasonable that it should be contained in our product -10° , especially since a considerable portion of this distillate condensed below -15° . In submitting 200 grams of this distillate in several portions to the action of chlorine with all possible precautions, a considerable portion of the chlorine product was lost, probably because it consisted to a large extent of the more volatile chlorine derivatives of propane. Although much of the unchanged hydrocarbon must have escaped with the gaseous hydrochloric acid, 100 grams remained after the chlorination, which was washed, dried, and distilled. Prolonged distillation, however, failed to collect any considerable portion within sufficiently close limits to indicate the presence in appreciable quantity of an individual hydrocarbon. A small quantity, perhaps 5 grams, collected between 65° and 70° , doubtless isobutane, which had not been completely removed into the higher fractions at 0° . But the product distributed itself along in degree fractions from 30° to 150° at no point in quantities larger than half a gram or one gram.

Between -10° and -2° much smaller quantities of the hydrocarbon distillates were obtained, but within the limits -2° and 2° , 300 grams came together, and the distillate -0° – 1° gave, as its specific gravity at 0° , 0.6029, and at -12° , 0.6141. Ronalds found as its specific gravity 0.6000. A vapor density determination gave the following value:—

0.0945 gram of the oil gave 73.6 c.c. of vapor at 5° , and under 370.4 mm. of mercury.

Calculated for C_4H_{10} .
2.01

Found.
2.07

In quantities of 100 grams each, the fractions -2° to 2° were converted into the chlorine derivatives. The chlorination of such a quantity is of necessity somewhat tedious; it requires continuous operation during ten or twelve days, and it cannot be hastened, since too rapid absorption generates heat, and rapid escape of hydrochloric acid carries off the pro-

* Ann. Chem. Pharm., CXLIV. 10.

duct. With care we were able to complete the absorption of sufficient chlorine without any considerable loss. In subjecting the chlorine product to fractional separation, after the fifth distillation it began to collect between 65° and 70° , and after the twentieth, 80 per cent collected at 68° – 69° . Of the remainder, 40 grams below 60° proved to consist mainly of unchanged hydrocarbon with sufficient chlorine product to raise the boiling point. Distillation of the higher portions was continued in 1° fractions to 160° , beyond which very little remained. To prevent a slight decomposition above 150° , at first distillation was conducted *in vacuo*; but the boiling points soon fell below the point of decomposition. In this entire series of 1° distillates, only at 120° – 121° did any appreciable quantity collect, and here only to the extent of 2 to 3 grams. The portions collected at other points were doubtless mixtures in very small amounts of higher chlorine products. The liquid 68° – 69° was shown by analysis and vapor density to have the composition required for monochlorbutane.

I. 0.1288 gram of the oil gave 0.2440 gram CO_2 , and 0.1166 gram H_2O .

II. 0.2025 gram of the oil gave 0.3845 gram CO_2 , and 0.1778 gram H_2O .

III. 0.2537 gram of the oil gave by the Carius method 0.3950 gram AgCl .

IV. 0.2645 gram of the oil gave 0.4078 gram AgCl .

	Calculated for $\text{C}_4\text{H}_9\text{Cl}$	Found.			
		I.	II.	III.	IV.
C	51.89	51.65	51.77		
H	9.73	10.06	9.76		
Cl	38.38			38.50	38.13

In a determination of its specific gravity at 24° , this butyl chloride gave 0.8690; at $27^{\circ}.8$, another determination gave 0.8648. The latter value agrees closely with that of Perin and Puchot,* who found at $27^{\circ}.8$, 0.8650.

In determining its vapor density by the method of Hofmann, 0.0975 gram of the oil gave 65 c.c. of vapor at 100° and under a tension of 36.44 mm.

Calculated for $\text{C}_4\text{H}_9\text{Cl}$	Found.
3.20	3.30

In further evidence of its identity, this butyl chloride was converted into the acetate by heating it twenty-four hours to 140° with fused

* Ann. Chem. and Pharm., CXXXVI. 1276.

potassic acetate and glacial acetic acid, according to the method of Schorlemmer. Upon diluting the contents of the tube, the oil which separated distilled for the most part at 116° – 117° , corresponding to the boiling point of isobutyl acetate, $116^{\circ}.5$. The acetate was converted into the alcohol by heating with alcoholic potassic hydrate, and its boiling point, 107° – 108° , showed it to be isobutyl alcohol, boiling point 108° – 109° . Upon analysis the alcohol gave the required percentages of carbon and hydrogen:—

0.1737 gram of the substance gave 0.4090 gram CO_2 , and 0.2113 gram H_2O .

	Calculated for $\text{C}_4\text{H}_9\text{OH}$.	Found.
C	64.86	64.22
H	13.51	13.52

Isobutyl sulphide was also prepared by boiling the chloride with an alcoholic solution of potassic sulphide. It gave the required percentage of sulphur:—

0.1640 gram of the oil gave by the method of Carius 0.2631 gram BaSO_4 .

	Calculated for $(\text{C}_4\text{H}_9)_2\text{S}$.	Found.
S	21.92	22.03

As already explained, prolonged fractional distillation failed to show the presence of any other chlorine derivative of this hydrocarbon except one that distilled tolerably constant at 121° – 122° . The quantity of this product was too limited to admit of complete purification; while the analyses showed that it still contained monochlorbutane, the results are sufficiently close to establish the presence of a dichlorbutane. Since no dichlorbutane with this boiling point has hitherto been found, it is to be regretted that our supply of material was so limited. But on account of the vast amount of labor that would be necessary to obtain an adequate quantity, it has not seemed of sufficient importance in the pressure of other portions of this work.

This substance gave the following results on analysis:—

I. 0.1390 gram of the oil gave by combustion with plumbic chromate 0.1960 gram CO_2 , and 0.1887 gram H_2O .

II. 0.2360 gram of the oil gave 0.5245 gram AgCl .

	Calculated for $\text{C}_4\text{H}_8\text{Cl}_2$.	I.	II.
C	37.79	38.46	
H	6.30	7.08	
Cl	55.91		54.94

The quantity of this product was insufficient for a determination of its specific gravity. The following value was obtained as its vapor density:—

0.1655 gram of the oil gave 87.2 c.c. of vapor at 182°, under a tension of 447 mm.

Calculated for $C_4H_9Cl_2$.
4.39

Found.
4.16

Our first attempts towards separating the butanes were made before the necessity of long continued distillation was fully appreciated. Not until after several trials was it observed to what an extent a small proportion of isobutane depressed the boiling point of pentane. In the earlier work, after six or eight distillations the product was assumed to be sufficiently pure for chlorination. A study of the chlorine derivatives showed beyond question that the hydrocarbon was pentane. We were still further misled by the boiling point of the pentyl chloride, 96°, which did not correspond to that of any hitherto published. Referring to our former notes on the vapor density of the distillate 8°–9°, we found the following determinations:—

- I. 0.0717 gram of the oil gave 45.5 c.c. of vapor at 16°, under a tension of 48.1 cm. of mercury.
- II. 0.0849 gram of the oil gave 46.8 c.c. of vapor at 18°.5, under a tension of 47.75 cm. of mercury.
- III. 0.0999 gram of the oil gave 51.5 c.c. of vapor at 18°.5, under a tension of 51.75 cm. of mercury.
- IV. 0.0751 gram of the oil gave 43.5 c.c. of vapor at 18°.5, under a tension of 45.76 cm. of mercury.

Calculated for
 C_4H_{10} C^3H_{12} .
2.01 2.49

Found.
I. II. III. IV.
2.04 2.38 2.35 2.36

It will be seen that determination I. corresponds closely to the composition of butane, and determinations II., III., and IV. to that of pentane. When these determinations were made, we expected results that would substantiate what had previously been done on the butanes, and therefore accepted only the first result, which was the last one obtained, as supporting this view. But in the light of further knowledge of these bodies, the determinations thought to be erroneous correspond more nearly to pentane, although showing the influence of the small quantity of isobutane. The first result was published in a former paper,* when

* These Proceedings, XXXI. 24.

it was assumed that we had in hand the butane which Warren had previously separated. Suspecting, therefore, the purity of our hydrocarbon distillate 8° – 9° , in resuming this work the distillation was conducted with a sufficient quantity of material, and carried far enough to separate completely all fractions between 5° and 20° . In the fraction 8° – 9° , after the tenth distillation, two vapor density determinations gave, (I.) 2.17, (II.) 2.17. In a distillate 6° – 8° , Ronalds * obtained as its vapor density 2.178, evidently indicating as our values do a mixture of butane and pentane.

But continuing this distillation in single degree fractions, scarcely anything remained within these limits after the twentieth distillation. Having obtained the same result in several quantities of forty-five litres each, collected at different dates, it became evident that neither Pennsylvania nor Ohio petroleum contains a single body with a boiling point between these limits. Furthermore, we have not been able to detect normal butane in any of these volatile distillates. There is not the least difficulty in separating chlorine derivatives of these hydrocarbons by fractional distillation. All the chlorine products we have prepared have collected readily within the limits of temperature of their characteristic boiling points. But in no instance in the chlorination of hydrocarbon distillates collected between -10° and 20° has a distillate collected at 77° – 78° , the boiling point of normal butyl chloride. Having excluded a constituent of Pennsylvania and Ohio petroleum within the limits mentioned above, and having observed that certain properties of isopentane derivatives are not in all respects identical with those previously published, it seemed to us of sufficient interest to devote some attention to the derivatives of this hydrocarbon. We therefore collected several hundred grams of a distillate at 29° – 30° , and exposed the oil to the action of chlorine in several separate quantities until about 200 c.c. of the substitution product was obtained. In generating such large quantities of chlorine, without discomfort from leaks, we have found the large Berlin porcelain stills extremely convenient. The chlorinated product was washed, dried, and carried through a long course of distillations, until after the eighteenth distillation it collected to the extent of 85 per cent between 95° and 96° , under a constant tension of 730 mm., which for convenience was selected for all these distillations. In a large series of distillations a constant tension is simply and very conveniently obtained by means of the tension regulator elsewhere described,† with the stopcock manipulated by a lever movable

* These Proceedings, XXXI. 10.

† Journ. Ch. Soc., 1865, p. 54.

on a horizontal support. By a suitable adjustment of side tubes, stopcocks and adapters, any number of distillation flasks may be introduced into the train, and regulated by the single stopcock. As many as fifteen distillations collecting in single degree fractions have been in simultaneous operation with no interruption incident to changes of flasks or collection of distillates. It is quite impossible, in Cleveland, to carry on a course of distillations extending through several weeks without some form of tension regulator, on account of sudden and extreme changes in the barometric pressure, occasionally equivalent to 25 mm. within a few hours.

Under 760 mm. and with the thermometer wholly in the vapor, chloropentane distilled completely between 96° and 97° , for the most part at $96^{\circ}.5$. From a distillate below 30° , Pelouze and Cahours obtained a butylchloride, as already mentioned, which boiled at 98° – 103° .

The purity of our product was shown by analysis: —

- I. 0.1205 gram of the oil gave 0.2479 gram CO_2 , and 0.1139 gram H_2O .
 II. 0.2166 gram of the oil gave 0.2952 gram AgCl .
 III. 0.2942 gram of the oil gave 0.4031 gram AgCl .

	Calculated for $\text{C}_5\text{H}_{11}\text{Cl}$	I.	Found. II.	III.
C	56.33	56.13		
H	10.33	10.51		
Cl	33.33		33.69	33.88

A determination of the specific gravity of this chloropentane at 20° gave 0.8750. Its vapor density by the Hofmann method was found to have the following value: —

0.1291 gram of the oil gave 72.6 c.c. of vapor at 100° , and under a tension of 384 mm.

Calculated for $\text{C}_5\text{H}_{11}\text{Cl}$	Found.
3.68	3.72

In forming isopentyl acetate, the purified chloride was heated 48 hours to 150° – 160° with potassic acetate and glacial acetic acid. When washed, dried, and well fractioned, a small quantity collected at 134° – 135° (760 mm.), which is somewhat lower than the boiling point of isoamyl acetate, $138^{\circ}.6$. The amount of our material was not sufficient to raise its boiling point, but it gave the required percentages of carbon and hydrogen.

0.1556 gram of the oil gave 0.3651 gram CO_2 , and 0.1514 gram H_2O .

	Calculated for $\text{C}_5\text{H}_{11}\text{C}_2\text{H}_5\text{O}_2$.	Found.
C	64.60	64.00
H	10.80	10.81

When heated during several hours with alcoholic potash, the acetate was converted into the alcohol which was separated from the solution with salt. On account of the small quantity of the alcohol obtained, its boiling point could not be raised above 117° – 120° (boiling point of inactive amyl alcohol 131°), although its composition corresponded to that of amyl alcohol.

0.1866 gram of the oil gave 0.4620 gram CO_2 , and 0.2293 gram H_2O .

0.1854 gram of the oil gave 0.4610 gram CO_2 , and 0.2315 gram H_2O .

	Calculated for $\text{C}_5\text{H}_{11}\text{OH}$.	Found.	
		I.	II.
C	68.18	67.51	67.81
H	13.63	13.66	13.88

At higher temperatures to 150° , the crude chlorine product could be distilled without decomposition. Above this point the residue was distilled *in vacuo*, which reduced the boiling point to such an extent that further distillation could be carried on under atmospheric pressure, leaving only a very small residue above 150° , probably of substitution products containing a larger number of chlorine atoms.

At no point between 96° and 160° could a distillate be held constant, except at 144° – 145° . Here 5 grams collected after the fifteenth distillation that distilled at 144° – 146° , mostly at 145° , under 760 mm. and with the mercury column wholly in the vapor. This oil proved on analysis to have the composition required for dichloropentane.

I. 0.1309 gram of the oil gave 0.2055 gram CO_2 , and 0.0888 gram H_2O .

II. 0.1976 gram of the oil gave 0.3993 gram AgCl .

	Calculated for $\text{C}_5\text{H}_{10}\text{Cl}_2$.	Found.	
		I.	II.
C	42.56	42.84	
H	7.09	7.54	
Cl	50.36		49.96

A determination of the vapor density of this body gave a value corresponding to dichloropentane.

0.1680 gram of the oil gave 80.6 c.c. of vapor at 182° , and under a tension of 426 mm.

Calculated for $C_6H_{10}Cl_2$

4.88

Found.

4.78

The boiling point of this dichloropentane is the same as that of amylene chloride, 145° , described by Bauer.* It is to be regretted that the quantity of our product was so limited; but on account of the great amount of labor involved in its preparation, it did not seem advisable to attempt the preparation of a larger amount.

These results indicate that petroleum contains but one butane, and that is isobutane, which collects at 0° . That this body is not normal butane is shown by the boiling point, 67° – 68° , of the monochlor derivative, the boiling point, 116° , of the acetate, that of the alcohol, 108° – 109° , and that of the sulphide, 172° . It has hitherto been assumed that the butane in petroleum is the normal hydrocarbon, because the butane prepared by Frankland from ethyl iodide and zinc boils at 0° . But isobutane prepared by Butlerow from tertiary butyl alcohol should boil at -17.5° . The differences between the properties of butane and isobutane are sufficiently marked to permit, without difficulty, of distinguishing between the isomeric forms.

Normal butyl chloride boils at $77^{\circ}.6$, and the alcohol at 117° . Since our series of derivatives from petroleum butane was prepared several times with the same results, and never with the formation of compounds with boiling points corresponding to normal butane, there can be no question that normal butane is not contained in Pennsylvania nor in Ohio petroleum. The serious question concerns the boiling point of isobutane which we found in petroleum. As has been fully explained, our 0° fractions were separated as many as four different times from the lightest gasoline we could procure from the refinery. While we never failed to collect distillates below -10° , they were much smaller in quantity than those in the vicinity of 0° . It is, therefore, certain that the butane we had in hand was isobutane, and it seems equally certain that this hydrocarbon collected at 0° and not at -17° .

THE OCTANES IN OHIO PETROLEUM.

It has already been pointed out by one of us (C. F. M., *loc. cit.*) that the published accounts of the octanes in petroleum are not fully

* Zeit. für Chem., 1866, p. 380.

concordant. Pelouze and Cahours first announced in their series of hydrocarbons an octane, boiling point 116° – 118° , and a little later Schorlemmer* found a body in coal tar distilling at 119° – 122° , and another at 124° , both with the composition required for octane. Possibly led to believe by the results of Beilstein and Kurbatoff that the distillate 119.5 – 122° is hexahydroisoxylol, in his later summation of the octanes known Schorlemmer seems to repudiate the one boiling at 119° – 122° , which he had previously described. Warren recognized two octanes, one boiling at 119.5 , and another boiling at 127.6 . These bodies were identified alone by vapor density determinations and boiling points; no analyses were given. In the separation of the hydrocarbons resulting from the distillation under pressure of menhaden oil, Engler discovered the octane, diisobutyl, boiling point 109° . In support of the work of Pelouze and Cahours, Lemoine† submitted American ligroine to four fractional distillations, collecting distillates within limits of five degrees, and separated an octane, boiling point 121° at 779 mm. In our experience, the hydrocarbons in petroleum with boiling points not far removed can only be separated by the use of the best possible means for fractional separation, in a long course of distillations. The separation of the octanes, for example, requires a refinery distillate boiling between 120° and 170° , and it is not until the twentieth distillation that the octanes begin to accumulate with any degree of purity. In all our experiments after the fifth distillation, the octanes are still contained for the most part in the portions above 125° , and they are separated very slowly into their respective fractions. In undertaking further study of the octanes in Ohio petroleum, we procured from the refinery of Messrs. Schofield, Shirmer, and Teagle 72 litres of a burning oil distillate that distilled in our hands, within the limits of ten degrees, in the following proportions:—

–75°	75°–100°	100°–110°	110°–120°	120°–130°	130°–140°	140°–150°	150°–160°	+160°
Litres 10	12	10	8	8	8	5	5	5

The sulphur compounds were precipitated from these fractions by means of alcoholic mercuric chloride, the oils washed and dried, and the distillation continued within limits of 5° , 2° , and finally within 1° , under a constant tension of 730 mm. In further explanation of what was said above concerning the slow separation of these constituents, the following record of the tenth distillation is given; when it is borne in mind that

* Jour. Chem. Soc., XV. 419.

† Bull. Soc. Chem., XLI. 161.

these weights are from 65 litres, the small amounts of the constituents will be appreciated: —

115°-116°	116°-117°	117°-118°	118°-119°	119°-120°	120°-121°	121°-122°
Grams 50	60	80	100	145	130	160
122°-123°	123°-124°	124°-125°	125°-126°	126°-127°	127°-128°	128°-129°
Grams 120	170	160	150	120	90	40

If the distillation had been stopped at this point, since on account of the diminished tension the true boiling points should be at least one degree higher than those given, it might be inferred that one of the principal constituents was a hydrocarbon boiling at 126°-127°.

No doubt this inference would be supported by the vapor density of this product, but further distillation showed its fallacy. At the end of the thirty-third distillation, 190 grams collected at 118°.5-119°.5, which distilled between 119°.5 and 120°, for the most part at 119°.5, under 760 mm. with the mercury column wholly in the vapor. Its specific gravity at 20° was found to be 0.7243. This liquid was assumed to have the same composition as the octane whose identity was shown by analysis and a vapor density determination.*

The vapor density of this product was found to support the same composition:—

0.1287 gram of the oil gave 75 c.c. of vapor at 182°, and under a tension of 429 mm.

Calculated for C_8H_{18} .
3.95

Found.
3.91

The specific gravity of the crude distillate was found to be 0.7256. The presence of this hydrocarbon is still further assured by the prolonged distillation. Our boiling point is practically the same as that of Warren, although his product from Pennsylvania petroleum must have been contaminated to some extent by hexahydroisoxylol, which was not shown to be present in Pennsylvania oil until long after the work of Warren was completed. Our boiling point was taken in a portion of the Ohio oil which had been subjected to prolonged treatment for the removal of hexahydroisoxylol. The specific gravity of this distillate purified by fuming sulphuric acid with the aid of heat was 0.7230. Another portion purified with a mixture of nitric and sulphuric acids gave as its specific gravity 0.7190. In the oil with

* Mabery, *loc. cit.*

the same boiling point separated from coal tar, Schorlemmer found the specific gravity 0.7190 at 17°.5. In our product purified with fuming sulphuric acid, the required percentages of carbon and hydrogen were obtained.

0.1475 gram of the oil gave 0.4562 gram CO_2 , and 0.2073 gram H_2O .

	Required for C_8H_{18} .	Found.
C	84.22	84.35
H	15.80	15.62

In the formation of chlorine derivatives from this octane, the same method was employed without cooling as in the case of the more volatile distillates. It was ascertained that the best yield of monochloroctane was given when the quantity of chlorine absorbed was 50 per cent in excess of the amount theoretically required to form the monochlor derivative. Even with this excess, still a small amount of the hydrocarbon remained unchanged. Since it was found that the chlorinated compound could not be distilled under atmospheric pressure without serious decomposition, after washing and drying it was fractioned *in vacuo* under a tension of 50 mm., within limits of 10°, 5°, 2°, and finally for some time within 1°. Under 50 mm. fractions collected at all points between 65° and 150°, but a larger quantity at 83°–84°, which under atmospheric pressure distilled at 164°–166°. The composition of this substance was determined by analysis:—

I. 0.1479 gram of the oil gave 0.3523 gram CO_2 , and 0.1537 gram H_2O .

II. 0.1961 gram of the oil gave 0.1888 gram AgCl .

III. 0.2483 gram of the oil gave 0.2408 gram AgCl .

	Calculated for $\text{C}_8\text{H}_{17}\text{Cl}$.	I.	Found. II.	III.
C	64.65	64.95		
H	11.45	11.54		
Cl	23.90		23.81	23.97

A determination of vapor density gave a value required for monochloroctane:—

0.1682 gram of the oil gave 78 c.c. of vapor at 182°, and under a tension of 400 mm.

Required for $\text{C}_8\text{H}_{17}\text{Cl}$.	Found.
5.14	5.28

The monochloroctane obtained by Pelouze and Cahours,* and by Schorlemmer,† from petroleum octane, boiling point 168° – 172° , was evidently a mixture of the two chloroctanes from the hydrocarbons $119^{\circ}.5$ and 124° . It could not be otherwise, on account of the imperfect separation of the hydrocarbons. In our experience, nothing less than thirty distillations is sufficient for the separation of these bodies with any degree of purity.

In comparing the results in this paper with those of others, it should be borne in mind that our products were separated from Trenton limestone petroleum, which was unknown at the time of the earlier study of Pennsylvania oil. But there can be little doubt that these portions of Pennsylvania and Ohio oils are identical so far as the principal constituents are concerned. That this is true of constituents with boiling points above 150° will be shown in another paper.

In many instances, even after the most careful purification, the specific gravity of the petroleum hydrocarbons is somewhat higher than that of the same hydrocarbons synthetically prepared. Schorlemmer‡ thought this was due to fine differences of isomerism. But this was before the discovery of naphthenes in petroleum. It now seems very probable that the higher specific gravity is due to the difficulty in removing the last trace of these bodies, especially since a small excess of carbon and a slight deficiency in hydrogen for the formula C_nH_{2n+2} accompanies the higher specific gravity. A notable quality of the naphthenes is their inertness toward reagents, which is doubtless greatly increased by large dilution in the principal petroleum hydrocarbons.

In Russian petroleum, Markownikoff and Putochin§ discovered isoctanaphene, boiling point $122^{\circ}.5$. In looking for this hydrocarbon in Ohio petroleum the fractions 120° – 124° were carefully distilled many times, until so little remained within these limits no individual constituent could be present in any appreciable quantity, or in such quantity that it could be collected by fractional distillation and identified. The octane found by Lemoine at 121° is, therefore, also excluded.

The octane, boiling point $125^{\circ}.46$, separated by Schorlemmer, was assumed to be identical with normal octane formed from normal butyl iodide by the action of sodium. Warren found a somewhat higher boiling point in the octane from Pennsylvania petroleum. This body

* Jahr. 1863, p. 528.

† Ann. Chem. Pharm., CXXV. 112.

‡ Phil. Trans., CLXXI. 451 (1880).

§ Ber. der deutsch. chem. Gesellsch., 1885, p. 1860.

distilled between $126^{\circ}.8$ and $129^{\circ}.1$, or in the mean at $127^{\circ}.6$; its composition was based upon a determination of its vapor density, but it was not supported by analysis. The observations of Warren were apparently confirmed by similar distillates separated from Ohio and Canadian petroleum.* Distillates collected at 126° – 127° from these oils after the eleventh fraction gave values in vapor density determinations corresponding to that of octane. But evidently such determinations, unsupported by other data, are less reliable, especially in products not far removed in boiling points from other isomers. Although our former results apparently confirmed the presence of an octane at 126° – 127° , those values were accepted as provisional, to be supported or modified by more prolonged distillations which have now been made.

Under a constant tension of 730 mm., forty-two distillations were made between 121° and 130° through Hempel bead columns. Of the last distillates scarcely any remained at 126° – 127° , or between this point and 130° , and very little at 125° – 126° . The greater portion, 200 grams, collected at 124° – 125° , normal conditions. There is, therefore, in Ohio petroleum, no octane with a boiling point higher than 125° . After purification with a mixture of nitric and sulphuric acids and sodium, the distillate 124° – 125° was shown by analysis to have the composition for octane.

0.1471 gram of the oil gave 0.4544 gram CO_2 , and 0.2077 gram H_2O .

	Calculated for C_8H_{18} .	Found.
C	84.22	84.26
H	15.79	15.70

After thorough treatment with fuming sulphuric acid, this octane gave 0.7183 as its specific gravity. Another portion, carefully purified with a mixture of nitric and sulphuric acids gave 0.7134. The specific gravity of the synthetic hydrocarbon was given by Thorpe as 0.7188. The crude distillate, with no purification, gave as its specific gravity 0.7243. Its vapor density was found by the method of Hofmann.

0.1578 gram of the oil gave 84.4 c.c. of vapor at 182° , and under a tension of 462 mm.

Calculated for C_8H_{18} .	Found.
3.95	3.96

In the formation of monochlorooctane from this distillate, the hydrocarbon was exposed to the action of chlorine in the cold until the

* Mabery, Proc. Amer. Acad., XXXI. 32, 57.

increase in weight was fifty per cent in excess of the quantity theoretically required to form monochlorooctane. The product, containing a small amount of the hydrocarbon still unchanged, was washed, dried, and submitted to fractional distillation *in vacuo* under 50 mm., since it was found that it could not be distilled under atmospheric pressure without decomposition. A considerable portion collected at 89°–91°, that distilled under atmospheric pressure, normal conditions, at 173°–174°. Schorlemmer stated that chlorine converts normal octane into a mixture of primary octyl chloride, boiling point 179°–180°, and secondary octyl chloride boiling at 175°. None of our product collected at the point corresponding to the normal chloride, although the quantity was not sufficient to determine the boiling point with absolute precision, and not sufficient to form other compounds. Pelouze and Cahours* gave 168°–172° as the boiling point of the chloride which they formed from petroleum octane, but their hydrocarbon was evidently not fully purified.

This substance gave upon analysis percentages of carbon, hydrogen, and chlorine required for chlorooctane: —

- I. 0.1222 gram of the oil gave 0.2880 gram CO_2 , and 0.1264 gram H_2O .
 II. 0.1821 gram of the oil gave 0.1792 gram AgCl .
 III. 0.2203 gram of the oil gave 0.2200 gram AgCl .

	Calculated for $\text{C}_8\text{H}_{17}\text{Cl}$.	I.	Found. II.	III.
C	64.65	64.27		
H	11.45	11.49		
Cl	23.90		24.33	24.69

A determination of vapor density gave a value required for chlorooctane: —

0.1675 of the oil gave 76 c.c. of vapor at 182°, and under a tension of 418 mm.

Calculated for $\text{C}_8\text{H}_{17}\text{Cl}$.	Found.
5.14	5.16

The small amount of distillates above 91° *in vacuo* showed the presence in minute proportions of higher chlorinated products, but it would require much larger quantities than we could conveniently procure to ascertain their composition.

* Jahr. Fittig, 1863, p. 528.

Since Engler* discovered tetramethylbutane or diisobutyl, boiling point 108.5° , as one of the products in the distillation of fats under pressure, with the possibility that this body might be present in Ohio petroleum, we submitted the portions of this petroleum distilling between 100° and 115° to prolonged distillation within single degree limits. But after treatment with nitric acid, no distillate collected in this vicinity. Having in hand a series of fractions near 135° – 136° , the boiling point of hexahydromesitylene, or mononaphtene, they were carried through a long course of distillations, and the small amount remaining within these limits was examined with the aid of fuming nitric acid and fuming sulphuric acid, but no sulphonic acid was formed, and the very small amount of nitro compound was not sufficient for a melting point.

In view of the fact that the series of petroleum hydrocarbons boiling approximately at 38° , 68° , and 98° , have received little attention since they were first discovered by Warren, I shall soon undertake an examination of these bodies, and also of petroleum nonane to which Warren assigned the boiling point 151° .

* Ber. der deutsch. chem. Gesellsch., 1889, p. 502.